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FEASIBILITY OF REMOVING TRANSITION METALS FROM LIQUID PROPELLANT SOLUTIONS BY CATHODIC REDUCTION

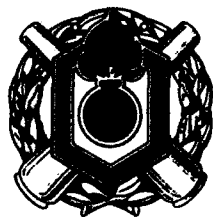R. Savinell
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FEASIBILITY OF REMOVING TRANSITION METALS FROM LIQUID PROPELLANT SOLUTIONS BY CATHODIC REDUCTION

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Electrochemical and some nonelectrochemical techniques were experimentally evaluated for removing trace quantities of iron and copper from hydroxyl ammonium nitrate solutions.

A high mass transfer packed bed electrochemical reactor was designed and built for removing the trace metals by cathodic plating. Several bed materials were evaluated including lead and amalgamated copper. Electrode potential and solution pH were the operating variables studied. Although cathodic plating of copper worked quite well with removal efficiency of 93%, iron was not so efficiently removed. It was determined that lead was unsuitable as a substrate, but amalgamated copper (and perhaps graphite) are still candidate substrate materials.

Both electrochemical and nonelectrochemical techniques for removing metal ions as a hydroxide precipitate were investigated. Some success appeared to be achieved using alumina as a coagulation agent at a pH of 3.1. These results have yet to be reproduced.

This report presents the details of the experiments and results of this research

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INTRODUCTION

The United States Army is currently investigating the properties of a group of liquid propellant solutions each of which contains hydroxylammonium nitrate (HAN) as an energy carrier (ref 1). It has been determined that the presence of trace heavy metal ions causes HAN decomposition and has a negative effect on the propellant's storage capacity and burning behavior (refs 1 and 2). The purpose of this contract was to ascertain if metal ions, particularly cupric and ferric ions, could be removed by electrochemical techniques.

There were several approaches taken in this research. Cathodic plating by electrochemical reduction was investigated. Research was also directed at evaluating the feasibility of hydroxide precipitation. Both electrochemical and nonelectrochemical experiments were performed.

BACKGROUND

A review of liquid propellants, their properties and physical characteristics, and their use in guns has been prepared by Klein (ref 1). In this review, reference is made to earlier studies which show that the stability of HAN is adversely affected by the presence of traces of transition metal ions, in particular, cupric ion, ferric ion, and nickle ion. Army sponsored projects have demonstrated some success in removing some of these ions by use of complex agents (ref 3) and ion exchange resins (ref 4)

THEORY

Equilibrium potentials for water, cupric ion, and ferrous ion reduction are shown in figure 1. These reactions are written as

$$H_2O + e --- 1/2H_2 + OH^-$$
$$Cu^{++} + 2e --- Cu^o$$

$$Fe^{++} + 2e --- Fe^o$$
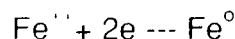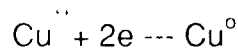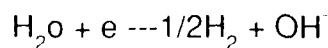
The ferric ion, which is probably the ionic iron species present in HAN solutions, will reduce the ferrous ions at a potential of about +0.529 V versus an SCE reference electrode. Therefore, ferric ion will first reduce to ferrous ion before iron plating occurs.

In order to reduce a species, the potential must be shifted in a direction more negative to the equilibrium potential. This overpotential must be sufficient to overcome activation and concentration effects.

As shown in figure 1, cupric ion reduction thermodynamically occurs prior to water reduction. However, experimental data are needed to determine if the overpotential necessary to drive practical reaction rates will force the electrode potential sufficiently negative into the water reduction region. Ferrous ion reduction has an equilibrium potential already negative to water reduction up to a pH of about 7.5. Therefore, water reduction is preferred in this case. However, the kinetics of water reduction on surfaces like zinc, lead, and mercury are slow, and a high overpotential is needed for significant reaction rates. Under certain conditions, it may be possible to reduce active species without significantly reducing the solvent. This forms the rational for performing the cathodic plating experiments in this research.

In solutions dilute in reactants, such as in the case of trace metal ions in HAN solutions, a high mass transfer rate is necessary to avoid low impractical limiting currents. Three-dimensional electrodes such as packed fluidized bed electrodes have been used to overcome this problem. A number of papers have been published which describe the theory and practice of these devices (refs 5 through 8).

In a solution of low acidity, the free hydroxide will combine with ferric ions to yield a nonsoluble precipitate according to the reaction:

$$2 \ FeOH^{++} + H_2O = Fe_2O_3 + 4 \ H^+$$
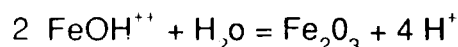
According to Purbaix (ref 9), the solubility of ionic species in a noncomplexing solution can be presses as

$$\log [\ FeOH^{++}] = 2.41 \ - \ 2pH$$

where the square brackets refer to molar concentration. In a solution of pH of 3.5, the ferric ion solubility is approximately 1.4 ppm. The precipitate in solutions of this type are colloidal gels which are difficult to remove by filtration or settling. However, the addition of flocculating agents such as alumina will cause the iron hydroxide precipitate to coagulate and separate from the solution (ref 10). An electrochemical technique of temporarily adjusting the HAN solution pH is shown in figure 2. After removing the hydroxide precipitate, the anolyte product can be combined with the treated catholyte and the final solution will again be acidic.

EXPERIMENTAL SYSTEM

Since it was known that the metal ion concentrations are low, a high mass transfer cell was employed in the form of a packed bed electrochemical reactor. The schematic diagram of the cell which was used for the experimental work (fig. 3) is constructed of lucite and is approximately 30 cm long. The bottom section is packed with 3 mm spherical beads and is 20.3 cm long and 5.08 cm in diameter. This ratio of bed length to bed diameter has been suggested for obtaining uniform flow by Perry (ref 11). The current collector plate is of the same material as the bed and is perforated with 1.6-mm holes. The bed is held in place by a lucite plate which is also perforated with 1.6-mm holes. The top section of the cell consists of the reference electrode capillary and counter electrode. The reference electrode (SCE) was kept external from the reactor during an experiment. A 1.6 mm Luggin capillary leading to a reference electrode chamber served as a bridge. The counter electrode was a DSA mesh electrode welded to a 6.4 mm titanium rod.

The flow system used for the experiments is shown in figure 4. A continuously stirred tank was used to hold the solution as it recirculated through the system. Nitrogen was sparged into the tank prior to an experiment to remove oxygen from the fluid. A sample port was attached to the tank to remove samples of fluid at specific time intervals during the experiment. PVC pipe (1/4 in.) was used for the piping since it is stable in HAN. A set of valves controlled the flow rate through the reactor which was measured by the flowmeter placed before the reactor. A thermometer monitored temperature changes in the fluid as the experiment progressed.

EXPERIMENTAL RESULTS

Bed Materials

Cathodic protection experiments were performed to determine which bed material would perform best under the process conditions (i.e., 2.8-M HAN).

Zinc was the first metal tested and was found to be very reactive in 2.8-M HAN and 11-M HAN. As soon as a metal sample (3 cm x 3.2 cm) was placed in 2.8-M HAN, a film formed on its surface. Since it was thought that the zinc may be dissolving, cathodic protection was tried by applying a potential of -1.0 V with respect to SCE. When the potentiostat was turned on, gas evolution was observed at the platinum counter electrode. and the zinc surface was observed to be still reacting. The potential was then set at -1.2 V versus SCE and no apparent change was noted. The current, at a potential of -1.0 V. was recorded as a function of time and found to be cathodic at the zinc electrode. It steadily decreased from 7.46 ma/cm^2 to 6.82 ma/cm^2 after about 6

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hours. In the next experiment, the zinc was weighed before and after cathodic protection (again at a potential of -1.0 V). The rate of weight loss over a 2-hour period was found to be 1.59 gm/hr (2.30×10^5 gm/cm^2-s). It appeared that zinc was too reactive for this application, so other bed materials were evaluated.

Lead was then tested as a possible bed material and found to be substantially more stable than zinc. Lead is known to have a high hydrogen overpotential. When a lead sample (3.8 cm x 0.8 cm) was placed in a 2.8-M HAN, no reaction was observed at the lead surface; however, there was gas evolution at the platinum counter electrode when the potential was set to -0.4 V with respect to SCE. There was a very slow decrease in anodic current from 5.84 mA/cm^2 to 5.45 mA/cm^2 over 3 hours. The open circuit poterntial for lead in 2.8-M HAN wsa found to be -0.47 V versus SCE. The potential was then controlled at -0.5 V where there was no reaction at the lead surface and no gas evolution at the platinum counter electrode. The rate of weight loss that occurred during this latter 2 hour experiment was 8.6×10^8 gm/cm^2-s. It appeared as though lead would be a good candidate material for further tests and was, in fact, the first material tested.

HAN Concentration Measurements

The HAN concentration was a critical factor for each experiment and therefore potentiometric titration was the method used in determining the molarity of HAN. It was believed that this method would be more accurate than gravimetric analysis. Typical titration curves for stock 2.8-m HAN using 1N NaOH as the titrant is shown in figure 5. The initial volume of the HAN was 80 ml, while the total volume of titrant added was 230 ml. Reproductibility was observed. The two inflection points were used to determine the volume of titrant for calculating HAN concentration. The following equation was used

$$V_t N_t = V_i N_i$$

where

N_t = 1N = 1M (NaOH)

V_i = 80 ml HAN

V_t = volume of titrant at second inflection point (200 ml)

volume of titrant at first inflection point (~ 0 ml)

N_i has units of moles HAN/liter. From the data shown in figure 5, a molarity of 2.75 was calculated. A value of 2.8 was specified by the manufacturer.

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Cyclic Voltammetry Studies

Some preliminary cyclic voltammetry experiments in 2.8 M HAN solutions were performed. The reference electrode was an SCE and was separated from the main compartment of the cell by use of a Luggin capillary. The counter electrode was a graphite rod which was isolated from the main compartment by a fritted glass disk. Two working electrodes were evaluated, platinum and glassy carbon. Although the solution was sparged with nitrogen before a voltammogram was taken, the cell was not airtight.

The voltammograms for the platinum disk electrode are reduced in figure 6. A significant oxidation current starts at +0.4 V (vs SCE). The currents are even larger for the reverse sweep which indicates a more complicated mechanism than simple oxidation reduction. The reduction peak starts at approximately -0.2 V which appears to be partially reversible H absorption. Hydrogen gas evolution appears to be beginning at -0.5 V. Both oxidation and reduction currents are dependent on the rotation rate of the disk electrode. This indicates that species in solution, such as HAN, are involved in the surface reaction.

The voltammograms for the glassy carbon disk electrode are reproduced in figures 7 and 8. In this instance, a small oxidation current starts at +0.5 V. In the cathodic direction there is only a small reduction current even at -0.1 V. There appears to be only a small dependency of current or rotation rate. The effect of scan rate is shown in figure 8. The voltammograms appear to be typical of what is expected for reversible double layer charging.

These results indicate that glassy carbon has a wide potential window of electrochemical inactivity in 2.8 M HAN. This information is encouraging since it indicates that HAN will not be reactive at potentials necessary for iron reduction. However, the presence of iron on the surface may compromise this effect. Further, cyclic voltammetry studies in air tight cells, with blank reference solutions, and at different surfaces are necessary for further elucidating the electrochemistry of HAN solutions.

Experiments with Cathodic Plating, Packed Bed of Lead Particles

Experiments with a packed bed of lead particles were begun to determine if iron ions could be cathodically removed from 2.8 M HAN solutions. The lower concentration of HAN was used in these studies because it was readily available. Further experiments with 11-M HAN could follow successes with the 2.8-M solution.

Runs USA2-PBL-1 and USA2- PBL-2

The first experiment was performed using 2.8-M HAN spiked with 50-ppm iron. Since a minimum potential of -0.82 V versus SCE was needed (as 1 ppm concentration) for iron reduction, a potential of -0.88 V was applied to obtain a driving force necessary for iron reduction. The results from the experiment are noted in table 1. The first and second experiments were run successively using the same solution. In this experiment, a potential of -0.96 V versus SCE was applied. These results are recorded in table 2. (Note: All iron concentrations were determined by atomic absorption analysis.)

Experimental Observations. It was observed throughout the experiments that the top layer of the bed turned a light grayish color while the middle and lower portions of the bed did not appear to change. As the experiments progressed, the grayish deposit at the top of the bed began to accumulate and separate from the bed itself. It was believed that the grayish deposit was actually an electrodeposited lead. This was thought to be the result of a nonuniform potential distribution along the length of the bed. Since the top of the bed was maintained at a cathodic potential by controlling it against the reference electrode, it is entirely possible that the bottom of the bed was sufficiently anodic to cause lead dissolution. The dissolved lead ions were then replated in the more cathodic regions near the top of the bed. In the next series of experiments the bed was considerably shortened.

Iron Removal Efficiency. In the first experiment, the initial iron concentration was 50 ppm which was reduced to ~45pm at the end of the experiment. This represents a 10% removal efficiency. In the second experiment, there was little additional removal efficiency.

pH and HAN Concentration Change. The pH solution dropped to a value of 1.9 at the end of the second experiment from an initial value of 2.6 which indicated that reactions other than proton or water reduction were occurring at the cathode. The final molarity of HAN was measured to be 2.37 M. It may be possible that a portion of the cathodic current went into reducing HAN. Also, the presence of iron ions may be responsible for the decrease in HAN concentrations. This possibility was examined further.

HAN Stability in the Presense of Iron. Since the concentration of HAN was deacreasing, it was necessary to determine if this decomposition was due to the presence of iron ions.

Stock 2.8-M HAN was spiked with 50 ppm iron and left idle for 22 hours to determine how the presence of iron effects HAN concentration. Samples of the solution were removed after 0, 2, 4, and 22 hours. These were each titrated with 1 N NaOh to measure the HAN concentration. It was found that the concentration ranged from 2.80 M to 2.69 M. With this small change in apparent concentration (most likely due to error

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in titration), the presence of iron did not seem to have a significant effect during the time of an experiment. More likley, the observed HAN concentration change during these two experiments was due to an electrochemical reaction.

Run USA2-PBL-3

This experiment was performed using 2.8-M HAN spiked with approximately 43-ppm iron. It differed from the earlier ones in that the bed length was shortened to one centir.eter. A potential of -0.965 V versus SCE was maintained on the bed in order to achieve iron reduction. These results are summarized in table 3. The current was cathodic which was primarily due to proton reduction observed during the run. From the concentration data, it was found that only 5% of iron was removed.

Run USA2-PBL-4

This experment was run with 2.8-M HAN spiked with 32-ppm copper. The purpose of the run was to determine if the system (reactor) was of proper design to remove trace metal ions from liquid propellant solutions. The results are reported in table 4. The potential of the bed was set to -0.305 V versus SCE. The current measured was anodic. Although copper was cathodically removed from solution, apparently at thye same time lead was anodically dissolving into solution. This was verified by the large lead concentration measured in the final solution. The copper removal efficiency was about 93% which was encouraging since it demonstrated that this reactor design was capable of removing trace metal ions. A plot of the copper concentration in the sump as a function of time is shown in figure 9, and figure 10 shows a plot of the data according to the theoretical expression given by Walker and Wragg (ref 12):

$$c_i(t) / c_i^0 = \exp (-t/T [1 - \exp (-kAaL/Q)])$$

where

$c_i (t)$ = ion concentration in sump at time t

c_i^0 = initial ion concentration in sump

t = time, s

T = residence time, V/Q, s

k = mass transfer coefficient, cm/s

A = cross sectional area of reactor, cm^2

a = specific surface area of electrode, cm^{1}

L = length of bed, cm

Q = volumetric flow rate, cm^3/s

V = volume of solution, cm^3

Based on this expression, the experimental data were used to estimate the mass transfer coefficient of the reactor under these operating conditions. A value of 4.6×10^3 cm/s was calculated which compared favorably to the value estimated by empirical correlation of Wilson and Gaenkoplis (ref 13).

Run USA2-PBL-5

The final run of this series was performed with 2.8-M HAN loaded with 36-ppm iron. However, prior to the experiment, the pH of the solution was raised to 4.8 by the addition of NaOH. The results are recorded in table 5. The potential was set to -0.975 V versus SCE. The current was cathodic which was mostly due to hydrogen gas evolution that was observed. As reported in table 5, iron was not removed from the solution.

Bed Evaluations. Since it was speculated that the lead bed was dissolving during these experiments, samples were taken after runs USA2-PBL-3 and USA2-PBL-4. It was found that the lead concentration after the first run was 2.28 gm/l and after titration to a pH of 12, it was reduced to 0.15 gm/l. For the other run, the lead concentration was 3.93 gm/l after the experiment and was reduced to 0.28 gm/l after titration to a pH of 12. The difference in the lead concentration between the two experiments was probably due to the fact that the potential in the second run was anodic to the lead equilibrium. The drop in the lead concentration after titration was due to lead precipitating out of solution as lead hydroxide. A white precipitate started to form at a pH of 6.4. It was thought at this point in time that lead was unsuitable for this application so other bed materials were tried.

Experiments with Cathodic Plating, Packed Bed of Amalgamated Copper Particles

Attempts were then made to cathodically remove iron from HAN solutions at an amalgamated copper bed. The rationale for this approach was that mercury has a high hydrogen overvoltage. The copper particles essentially served as a substrate for the mercury to give a larger area-to-volume ratio. It was thought that the plated iron would become imbedded in the mercury thus not exposing it to the strong oxidizing HAN solution.

Run USA2-AC-1

This experiment was perfomed with 2.8 M-HAN spiked with 45 ppm iron. The bed material was amalgamated copper particles which varied in diameter from 0.3 to 0.5 cm. The procedure used to amalgamate the copper for runs USA2-AC-1, USA2-AC-2, and USA2-AC-3 was:

1. Clean the copper surface with detergent and rinse

2. Dip the copper in dilute nitric acid for 2-3 minutes

3. Place the copper in the pool of mercury for 45 minutes

4. Store the amalgamted copper under water

A potential of -0.96V vs. SCE was applied to the bed. The results are reported in table 6. It was found that only 9% of the iron was removed from solution.

Run USA2-AC-2

This experiment was run successively to USA2-AC-1. All operating conditions remained the same except that the potential was raised to -1.30 V versus SCE. These results are summarized in table 7. There was no additional iron removal during this run.

With no encouraging results from the previous two experiments, another run with amalgamated copper particles was performed to investigate if a more basic pH (e.g., pH = 4) would accelerate the plating reaction while slowing water reduction.

Run USA2-AC-3

In this experiment, the initial solution was 2.8-M HAN with about 50-ppm iron at a pH of 4.04. The bed was amalgamated copper. The purpose of the experiment was to encourage iron deposition by offering a more favorable environment. It is known from literature that an increase in pH advances the kinetic rate of iron deposition. The results of the experiment are summarized in table 8. There was still virtually no iron removed. A different approach to cathodic plating was the pursued.

Electrochemical Hydroxide Precipitation Experiments

Since the results of cathodic plating of iron were not encouraging, constant current experiments were pursued. The purpose of these experiments was to reduce water at cathode particles and thus generate a high local pH. The concept was to precipitate the iron out as a hydroxide in the vicinity of the electrode surface. It was thought that an electrochemical precipitation process would avoid the necessity of significantly adjusting the bulk solution pH. This had been done in other work by the P.I. but with nickel.

Run USA2-CCC-1

This experiment was run with 2.8-M HAN at a pH of 1.34 with 60-ppm iron. The bed material was copper. The current was kept constant while the potential varied. The conditions and results are recorded in table 9. There was no iron removal during the run.

Run USA2-CCC-2

The purpose of this run was the same as for USA2-CCC-1 except that a larger current was applied. The results are summarized in table 10. Again, iron was not removed.

One possible reason for the failures of the electrochemical precipitation experiments was that the solution moved through the cathode and the past the anode where protons are generated. The success with the nickel work could have been the result of using a flow-by electrode where the anolyte and catholyte are separated. Also, in that system, the catholyte passed through a cyclone where solid hydroxide precipitates were removed before the solution returned to the sump.

Nonelectrochemical Hydroxide Precipitation Experiments

One liter of 2.8-M HAN loaded with approximately 50-ppm iron was titrated with NaOH to pH values of 2, 4, 6, and 6.8 in order to determine if iron could be removed from the solution as iron hydroxide precipitate. The results are tabulated below:

pH	Iron (Fe) concentration, ppm
2.05	35.9
4.00	34.4
5.90	29.4
6.80	1.9

As can be seen, iron was removed from the solution.

With these encouraging results, attempts were made to remove iron from 2.8-M HAN solutions by the use of pH and temperature effects. The following is a summary of the experiments performed. A short explanation of each experiment is presented followed by results of analysis of HAN and iron concentrations.

1. The first experiment was performed at room temperature to determine how an increase in pH, from 1.07 to 4.0, would affect HAN iron concentration. The solution was left idle for 5 days and then centrifuged for 15 min at 3000 rpm. The top layer was then drawn off, analyzed for iron by AA (atomic absorption), and titrated to measure the HAN concentration. The following is a summary of the findings:

Temperature	Room
Initial HAN molarity	2.80
Final HAN molarity	2.25
Initial Fe ppm	70

Final Fe ppm   57
pH   4.0

2. This experiment was performed at 5 ^{o}C to determine how an increase in pH, from 1.2 to 4.0, at lower temperatures would affect HAN and iron concentration. It was thought that the decrease in temperature might slow HAN decomposition. The solution was left idle for 5 days at the lower temperature and then centrifuged for 15 min at 3000 rpm. The following summarizes the findings:

Temperature	5 ^{o}C
Initial HAN molarity	2.80
Final HAN molarity	2.25
Initial Fe ppm	50
Final Fe ppm	48
pH	4.0

3. This experiment was similar to the second experiment except that the pH was raised to 6.0 from an initial pH of 1.2. This was done to encourage iron removal through iron hydroxide precipitation. The solution was kept at 5 ^{o}C for 5 days and then centrifuged for 15 min at 3000 rpm. The following summarizes the findings:

Temperature	5 ^{o}C
Initial HAN molarity	2.80
Final HAN molarity	0.50
Initial Fe ppm	50
Final Fe ppm	17
pH	6.0

4. In this experiment, the pH was raised from 1.2 to 4.0 at room temperature and then centrifuged within the hour. After centrifuging, nitric acid (1 ml) was added to lower the pH back to 2.0. The purpose was to determine if the separation could be affected in a short time without significant decomposition of the HAN solution. The solution was left idle for 3 days at the lower pH and then analyzed for iron and HAN concentration. The results are summarized as follows:

Temperature	Room
Initial HAN molarity	2.80
Final HAN molarity	2.20
Initial Fe ppm	70
Final Fe ppm	65
pH	4.0

5. This experiment was similar to the fourth experiment except that the pH was raised to 6.0 instead of 4.0. The solution was then promptly centrifuged. Nitric acid (3 ml) was added to lower the pH back to 2.0. The solution was left idle for 3 days at the lower pH and then analyzed for iron and HAN concentrations. The results are:

Temperature	Room
Initial HAN molarity	2.80
Final HAN molarity	2.20
Initial Fe ppm	70
Final Fe ppm	26
pH	6.0

From the above data , it seemed that there was a trade-off between HAN decomposition and iron removal. In both cases where there was significant iron removal, there was also significant HAN decomposition. This was true for both room temperature and lower temperature (5°C) conditions. It was also found that raising the pH to a value of six resulted in substantial iron removal. These results are consistent with the initial pH effect experiment that was performed prior to this series of experiments.

Nonelectrochemical Coagulation Experiments with Alumina

The removal of iron ions from weil water by using coagulation agents such as aluminum hydroxide is discussed in reference 14. Attempts were then made to remove iron from 2.8- HAN solutions with an alumina coagulation agent. In all the experiments, the pH was raised to 3 to 4 to create a favorable environment for metal hydroxide precipitation. The following described the experiments performed and gives an explanation and results.

1. In this experiment, the pH was raised to 3.1, and the solution was stirred overnight to provide intimate contact between the iron and coagulation agent. A sample, taken before the alumina was added, was centrifuged and found to contain 92-ppm iron by AA analysis. After the alumina was added (0.02 g / 100 ml solution), the iron concentration was measured to be 0 ppm.

2. This experiment was similar to the above except that the pH was raised to 4.0. AA analysis indicated that the iron concentration was 127 ppm before the alumina was added. After the alumina addition, there was a slight decrease in iron concentration to 122 ppm.

There appeared to be some success in removing the iron in the first experiment attempted; therefore, reproduction of these results was attempted. The experiments performed and the results obtained are given below.

1. A blank solution experiment was performed where no iron was purposely added to determine if iron was introduced during another point in the experiment such as during dilution before AA analysis. In this experiment, the pH was raised to 3.03 and the solution was mixed with the alumina for 4 hrs. The initial iron concentration was 2.7 ppm. The final iron was found to be 3.2 ppm which suggests that there was a small amount of iron introduced with the distilled water during dilution. However, this would not account for the results of the second experiment above.

2. In this experiment, the pH was raised to 3.1 and mixed with alumina for 4 hrs. The initial iron concentration was 56 ppm. The final iron concentration after alumina addition and centrifugation was 51 ppm.

Although the above results provide some indication of success with this approach, reproducibility has not been achieved. Further work must be done with coagulation agents to determine if the initial experimental results are indeed valid.

CONCLUSIONS

This research indicates that copper can be removed effectively from 2.8-M HAN solutions by cathodic plating in a packed bed electrochemical reactor. However, the removal of iron by cathodic plating, or otherwise, still presents a challenge.

At this time, the results of this research suggest a few routes (other than ion exchange) for removing iron from HAN solutions.

1. Cathodic reduction under very controlled and specific conditions, which must be identified.

2. Reduction of ferric ion to ferrous ion followed by stabilization of the ferrous ion with a chelating or stabilizing agent.

3. Enhancing precipitation at a pH of 3.5 to 4.0 by use of coagulation agents, adsorption, or temperature effects.

Since the earlier work with cathodic plating did not yield encouraging results, it appears as though a significant research effort would be required to pursue this approach. However, the second and third approaches may be evaluated with a more modest effort.

Table 1. Run USA2-PBL-1

Run USA2-PBL-1   Run Date 7/19/85

  Bed Properties   Solution Properties

Particle Size   0.25 cm   Electrolyte Volume   4000 cm^3

Bed Material   Lead   Flow Rate   35 cm^3/s

Bed Length   3.8 cm   Initial HAN Molarity 2.8

Estimated Bed   Final HAN Molarity   ----
Porosity   0.31
                               Initial HAN pH   2.60
Calculated Specific
Surface Area   16.56 cm-1   Final HAN pH   ----

Additional Notes: The final molarity and final pH of the
solution were determined after the second experiment.

time (min)	current (mA)	E vs. SCE	Fe (ppm)
0	290	-0.886	50
5	350	-0.885	47.4
10	390	-0.884	46.1
15	400	-0.883	44.3
20	440	-0.882	44.6
25	340	-0.886	44.3
30	560	-0.877	44.8
35	640	-0.875	46.2
40	700	-0.873	47.4
45	810	-0.869	45.9
50	810	-0.869	42.4
55	840	-0.868	41.3
60	840	-0.868	45.0

Nitrogen was sparged into the system during the experiment.
The tank mixer was not used because a coupling for the mixer has
not been received from Ace Glass.

Table 2. Run USA2-PBL-2

Run USA2-PBL-2   Run Date 7/19/85

Bed Properties   Solution Properties

Particle Size   0.25 cm   Electrolyte Volume   4000 cm^3

Bed Material   Lead   Flow Rate   35 cm^3/s

Bed Length   3.8 cm   Initial HAN Molarity ----

Estimated Bed   Final HAN Molarity   2.37
Porosity   0.31
                                        Initial HAN pH   ----
Calculated Specific
Surface Area   16.56 cm-1   Final HAN pH   1.90

Additional Notes: The temperature throughout both experiments
remained constant at 26 - 27 degrees Celcius.

time (min)	current (mA)	E vs SCE	Fe (ppm)
0	760	-0.967	45.0
17	890	-0.962	37.4
30	940	-0.960	45.5
40	960	-0.959	37.4
50	990	-0.958	45.7
60	1020	-0.957	44.9

Nitrogen   was   sparged   into   the   system   throughout   the
experiment.   The   ppm levels taken at 17 and 40 minutes are   not
considered reliable data probably because of error in dilution.

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Table 3. Run USA2-PBL-3

Run USA2-PBL-3   Run Date 8/14/85   Notebook Reference USA2-58

Bed Properties   Solution Properties

Particle Size	0.25 cm	Electrolyte Volume	4000 cm^3
Bed Material	Lead	Flow Rate	25 cm3/s
Bed Length	1.0 cm	Initial HAN Molarity	2.75
Estimated Bed		Final HAN Molarity	2.68
Porosity	0.31	Initial HAN pH	2.34
Calcualted Specific		Final HAN pH	2.139
Surface Area	16.56 cm-1		

Additional Notes: The temperature throughout the 5 hour experiment ranged from 28 to 31 degrees Celsius.

time (min)	current (mA) (cathodic)	E vs. SCE	Fe (ppm)
0	160	-0.888	43.0
20	170	-0.888	43.54
40	220	-0.965	42.38
60	230	-0.964	41.48
80	230	-0.964	44.18
100	240	-0.963	42.25
120	240	-0.963	41.51
140	240	-0.963	38.33
160	240	-0.963	41.13
180	240	-0.963	42.72
200	240	-0.963	42.21
220	240	-0.963	40.76
240	240	-0.963	40.64
260	260	-0.962	40.78
280	370	-0.955	40.70
300	490	-0.948	41.16

Nitrogen was sparged into the system for 45 minutes prior to the experiment. The solution was not mixed during the run because of enhanced turbulence in the tank. However, this problem was corrected for Run USA2-PBL-5.

Table 4. Run USA2-PBL-4

Run USA2-PBL-4   Run Date 8/20/85   Notebook Reference USA2-59

Bed Properties

Particle Size	0.25 cm
Bed Material	Lead
Bed Length	1.0 cm
Estimated Bed Porosity	0.31
Calculated Specific Surface Area	16.56 cm-1

Solution Properties

Electrolyte Volume	4000 cm^3
Flow Rate	25 cm^3/s
Initial HAN Molarity	2.75
Final HAN Molarity	2.65
Initial HAN pH	2.30
Final HAN pH	2.575

Additional Notes: The temperature throughout the experiment rose from 25 to 27 degrees Celsius.

time (min)	current (mA) (anodic)	E vs. SCE	Cu (ppm)
0	70	-0.305	32
20	60	-0.305	20.8
40	54	-0.305	13.24
60	40	-0.304	8.91
80	29	-0.304	5.25
100	20	-0.303	3.32
120	18	-0.303	2.21

Nitrogen was sparged into the system for 30 minutes prior to the experiment. The solution was not mixed throughout the experiment.

Table 5. Run USA2-PBL-5

Run USA-PBL-5   Run Date 8/22/85   Notebook Reference USA2-60

   Bed Properties   Solution Properties

Particle Size 0.25 cm   Electrolyte Volume   4750 cm^3

Bed Material   Lead   Flow Rate   25 cm^3

Bed Length   1.0 cm   Initial HAN Molarity 2.27

Estimated Bed   Final HAN Molarity   ----
Porosity   0.31
                             Initial HAN pH   4.78
Calculated Specific
Surface Area   16.56 cm-1   Final HAN pH   ----

Additional Notes: The temperature throughout this 3 hour
experiment varied from 26 to 27 degrees Celsius. A
potentiometric titration was not performed on the final solution
of this run.

time (min)	current (mA) (cathodic)	E vs. SCE	Fe (ppm)
0	169	-0.975	36
20	172	-0.971	36.1
40	178	-0.972	35.9
60	187	-0.971	37.3
80	190	-0.972	36.8
100	188	-0.973	36.2
120	185	-0.973	36.0
140	192	-0.973	36.7
160	199	-0.973	37.6
180	198	-0.974	37.0

   Nitrogen was sparged into the system 30 minutes prior to the
experiment and the solution was mixed throughout the run.

Table 6. Run USA2-AC-1

Run USA2-AC-1   Run Date 8/30/85   Notebook Reference USA2-68

Bed Properties

Particle Size 0.3 - 0.5 cm

Bed Material   Amalgamated Copper

Bed Length   1.0 cm

Estimated Bed
Porosity   0.31

Calculated Specific
Surface Area   10.35 cm-1

Solution Properties

Electrolyte Volume   3500 cm^3

Flow Rate   22 cm^3/s

Initial HAN Molarity 2.70

Final HAN Molarity   2.56

Initial HAN pH   1.67

Final HAN pH   1.53

Additional Notes: The temperature throughout the experiment
remained constant at 25 degrees Celsius.

time (min)	current (mA) (cathodic)	E vs. SCE	Fe (ppm)
0	180	-0.960	45
20	137	-0.965	43
40	135	-0.966	42
60	139	-0.968	41
80	135	-0.969	42
100	138	-0.970	42
120	137	-0.970	41

Nitrogen was sparged into the system for 30 minutes prior to the
experiment and the solution was mixed throughout the run.

Table 7. Run USA2-AC-2

Run USA2-AC-2   Run Date 8/30/85   Notebook Reference USA2-68

Bed Properties   Solution Properties

Particle Size   0.3 - 0.5 cm   Electrolyte Volume   3500 cm^3

Bed Material   Amalgamated Copper   Flow Rate   22 cm^3/s

Bed Length   1.0 cm   Initial HAN Molarity 2.56

Estimated Bed   Final HAN Molarity   2.45
Porosity   0.31
                                  Initial HAN pH   1.53
Calculated Specific
Surface Area   10.35 cm-1   Final HAN pH   1.53

Additional Notes: The temperature throughout the experiment
remained constant at 25 degrees Celsius.

time (min)	current (mA) (cathodic)	E vs. SCE	Fe (ppm)
0	191	-1.305	41
20	190	-1.305	42
40	207	. -1.305	42
60	209	-1.305	42

This run was run successively to run USA2-AC-1. Nitrogen was not
sparged into the system prior to this run. The solution was
mixed during the run.

Table 8. Run USA2-AC-3

Run USA2-AC-3   Run Date 9/25/85   Notebook Reference USA2-74

Bed Properties

Particle Size 0.5 cm

Bed Material Amalgamated Copper

Bed Length   1.0 cm

Estimated Bed
Porosity   0.31

Calculated Specific
Surface Area   8.28 cm-1

Solution Properties

Electrolyte Volume   4000 cm^3

Flow Rate   25 cm^3/s

Initial HAN Molarity 2.75

Final HAN Molarity   2.25

Initial HAN pH   4.04

Final HAN pH   1.302

Additional Notes: The temperature throughout the experiment remained constant at 25 degrees Celsius.

time (min)	current (mA)	E vs. SCE	Fe (ppm)
0	173	-1.18 V	48
15	166	-1.19 V	47
30	165	-1.19 V	48
45	171	-1.19 V	48
60	176	-1.19 V	47
75	174	-1.19 V	46
90	177	-1.19 V	45
105	180	-1.19 V	46
120	179	-1.19 V	46

Nitrogen was sparged into the system 30 minutes prior to the experiment. The solution was mixed during the run.

Table 9. Run USA2-CCC-1

Run USA2-CCC-1   Run Date 9/21/85   Notebook Reference USA2-72

Bed Properties   Solution Properties

Particle Size   0.4 cm   Electrolyte Volume   3900 cm^3

Bed Material   Copper   Flow Rate   25 cm^3/s

Bed Length   1.0 cm   Initial HAN Molarity 2.8

Estimated Bed   Final HAN Molarity   2.19
Porosity   0.31
                                        Initial HAN pH   1.34
Calculated Specific
Surface Area   10.35 cm-1   Final HAN pH   0.875

Additional Notes: The temperature throughout the experiment
remained constant at 24 degrees Celsius.

time (min)	current (Amps.)	E vs. SCE (Reference),V	Cell Voltage,V	Fe (ppm)
0	4.33	-10.23 V	15.36 V	63
5	4.33	-9.04 V	14.54 V	64
10	4.33	-8.89 V	14.15 V	63
15	4.33	-8.65 V	13.82 V	64
20	5.56	-10.70 V	16.77 V	60
25	5.56	-10.45 V	16.38 V	63
30	5.56	-10.40 V	16.24 V	64
35	6.85	-11.98 V	18.60 V	66
40	6.85	-11.77 V	18.22 V	69
45	6.85	-11.39 V	17.60 V	69

Nitrogen was sparged into the system 30 minutes prior to the
experiment.   The solution was mixed during the run.

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Table 10. Run USA2-CCC-2

Run USA2-CCC-2   Run Date 9/25/85   Notebook Reference USA2-74

Bed Properties   **Solution Properties**

Particle Size   0.5 cm   Electrolyte Volume   4000 cm^3

Bed Material   Copper   Flow Rate   25 cm^3/s

Bed Length   1.0 cm   Initial HAN Molarity 2.25

Estimated Bed   Final HAN Molarity   2.25
Porosity   0.31
                                   Initial HAN pH   1.302
Calculated Specific
Surface Area   8.28 cm-1   Final HAN pH   1.012

Additional Notes: The temperature throughout the experiment remained constant at 27 degrees Celsius. This experiment was run successively to USA2-AC-3.

time (min)	Current (Amps)	E vs. SCE (Reference),V	Cell Voltage,V	Fe (ppm)
0	8.06	-11.55	13.02	46
10	8.06	-11.07	12.55	47
20	8.06	-10.93	12.33	47
30	8.06	-10.71	12.13	47
40	8.06	-10.50	11.80	47
50	8.06	-10.25	11.54	47
60	8.06	-10.14	11.48	47

Nitrogen was not sparged into the solution prior to the experiment. The solution was mixed during the experiment.
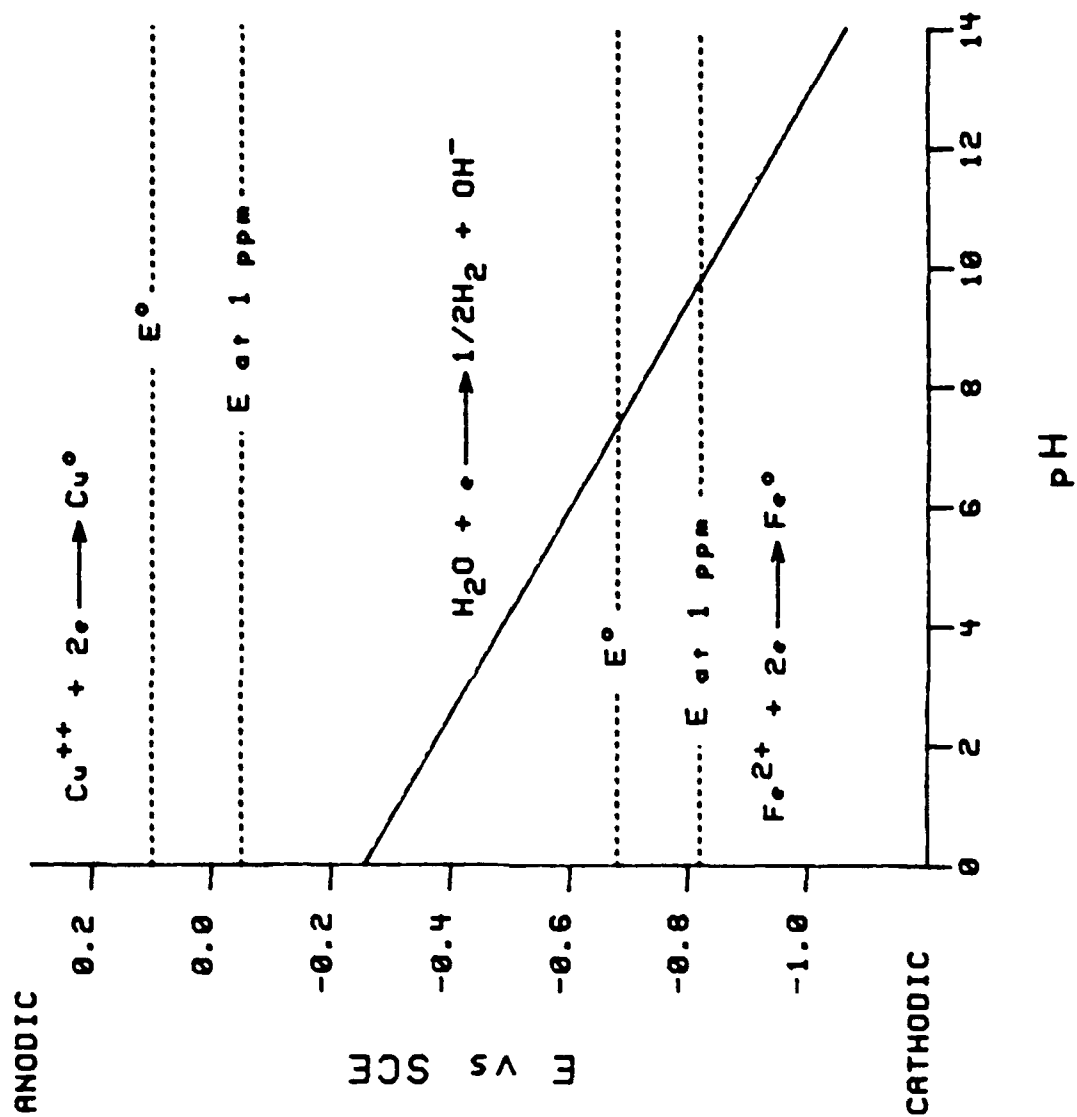
Figure 1. Thermodynamic stability of cupric and ferrous ions in aqueous solutions
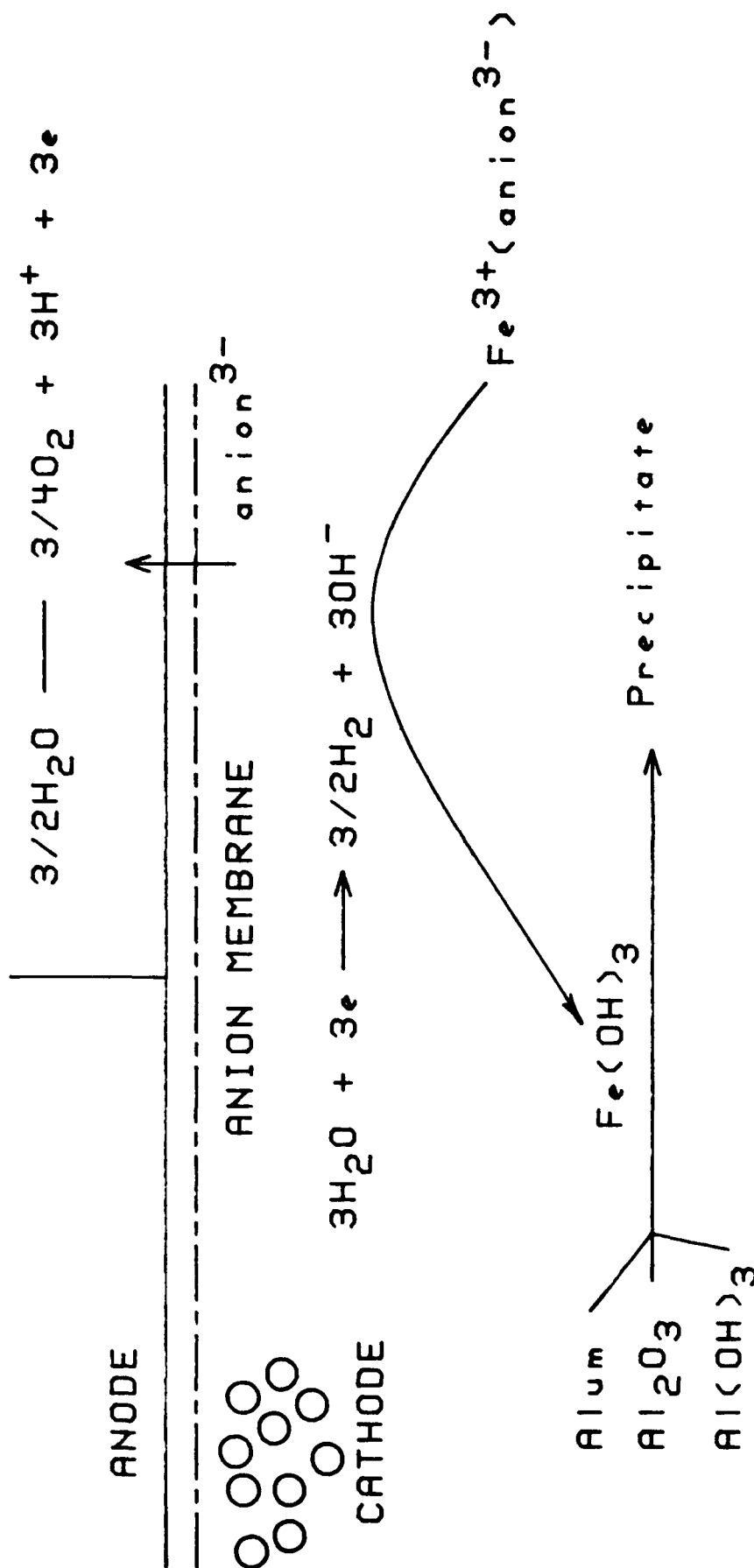
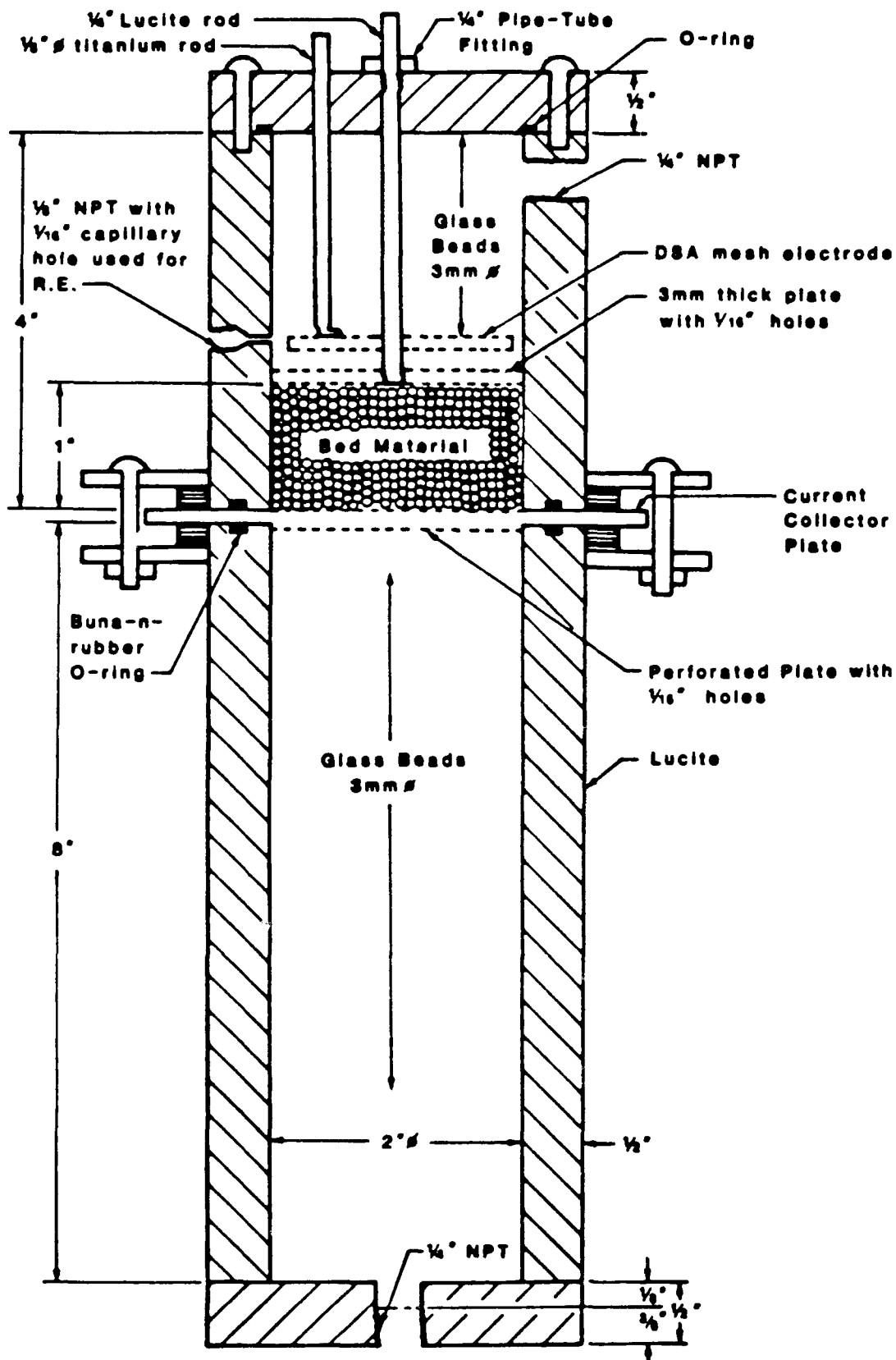Figure 2. An electrochemical technique for adjusting pH of HAN solutions

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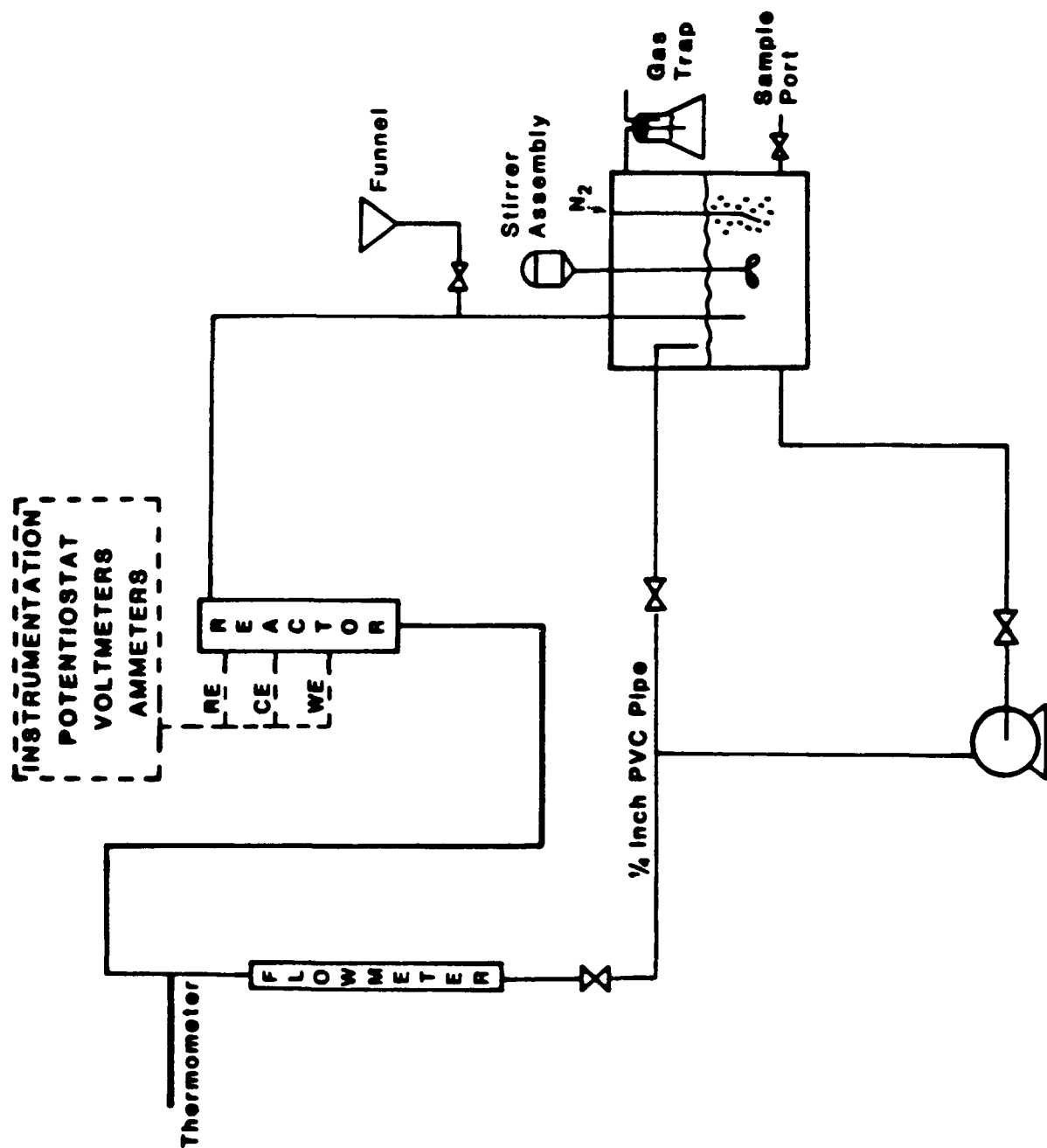Figure 3. Packed bed electrochemical reactor
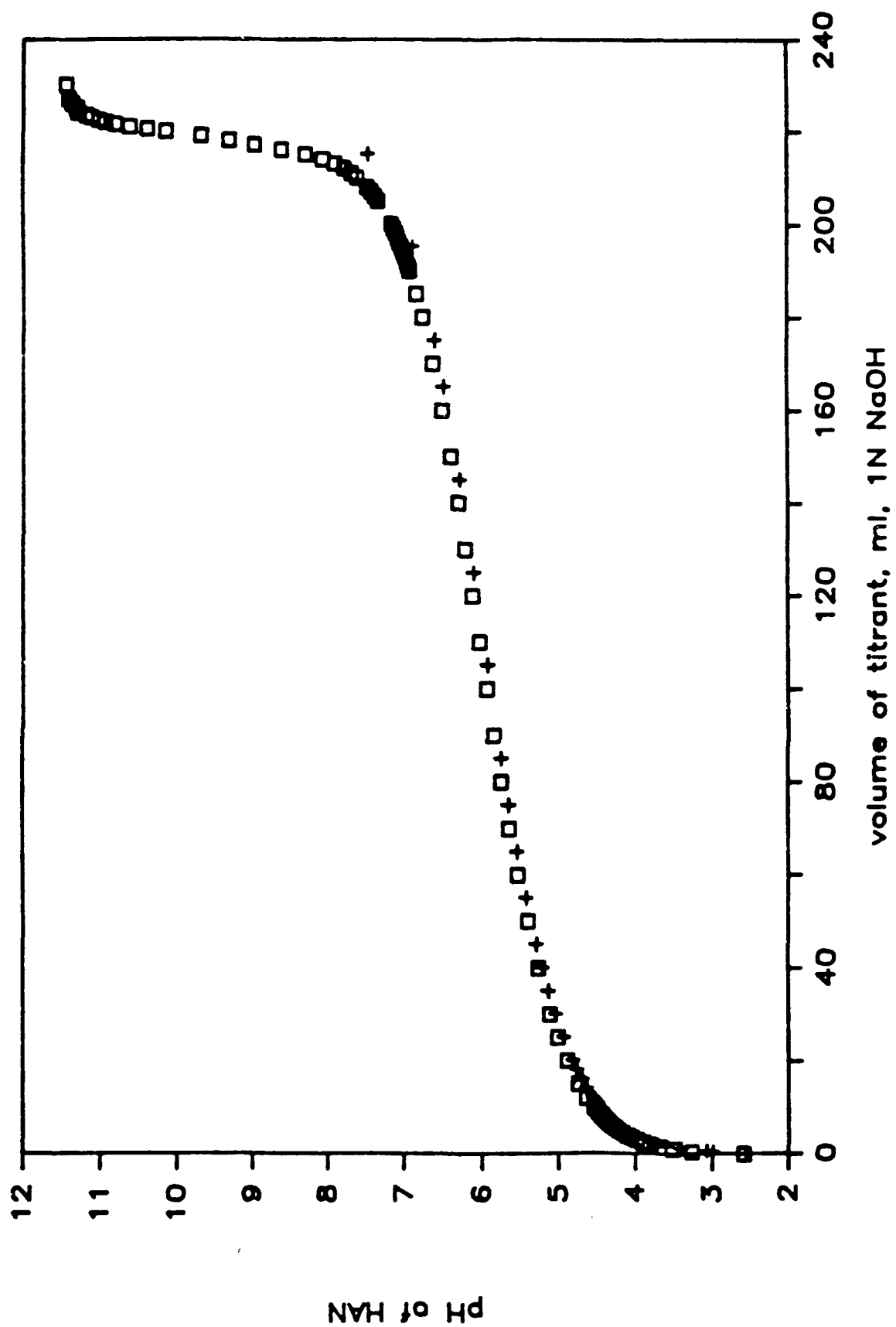
Figure 4. Process flow system

28

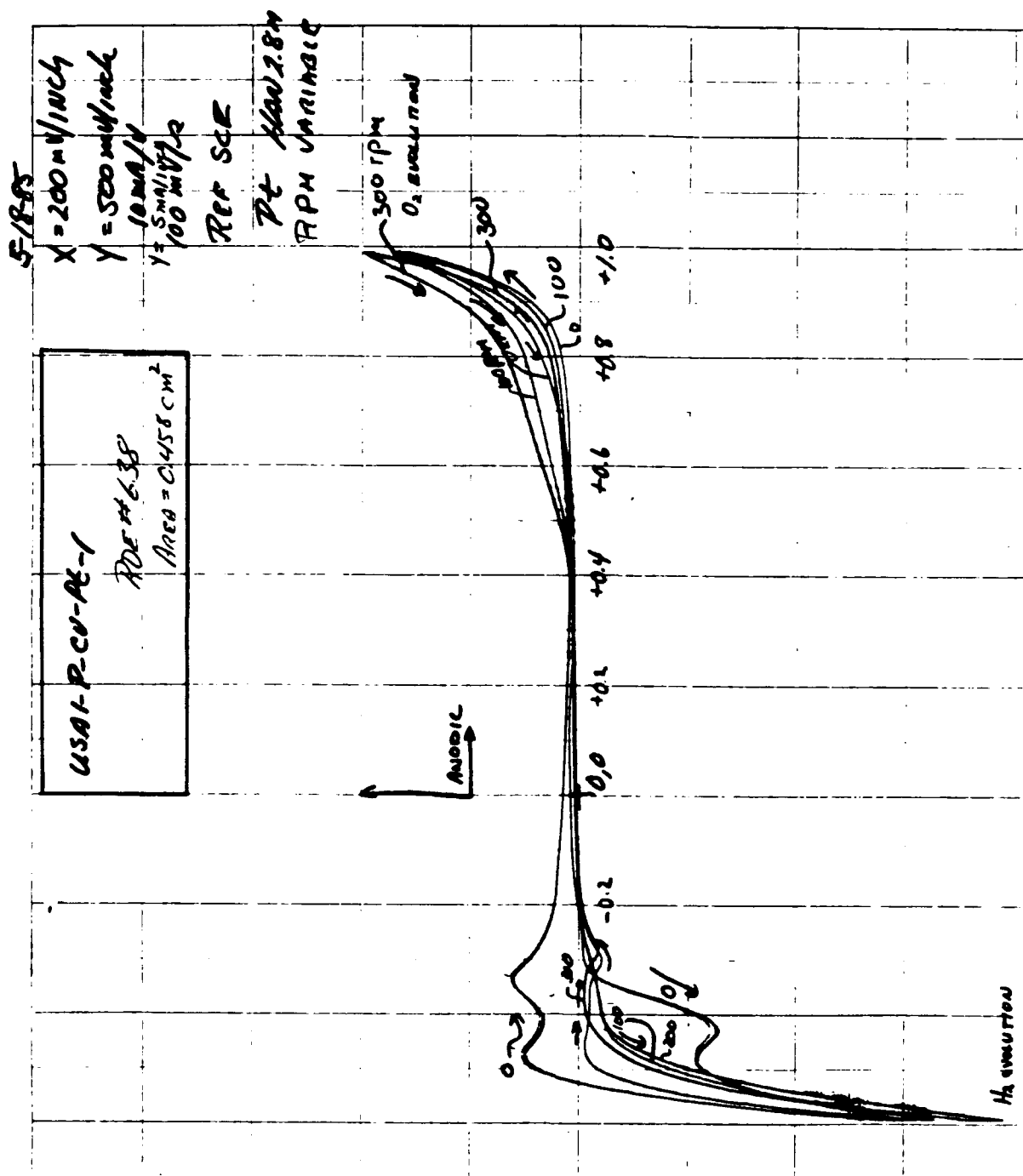Figure 5. ph of HAN versus volume titrant (different symbols represent two titrations)

Figure 6. Cyclic voltammetry of platinum electrode in 2.8M HAN with various rotation rates

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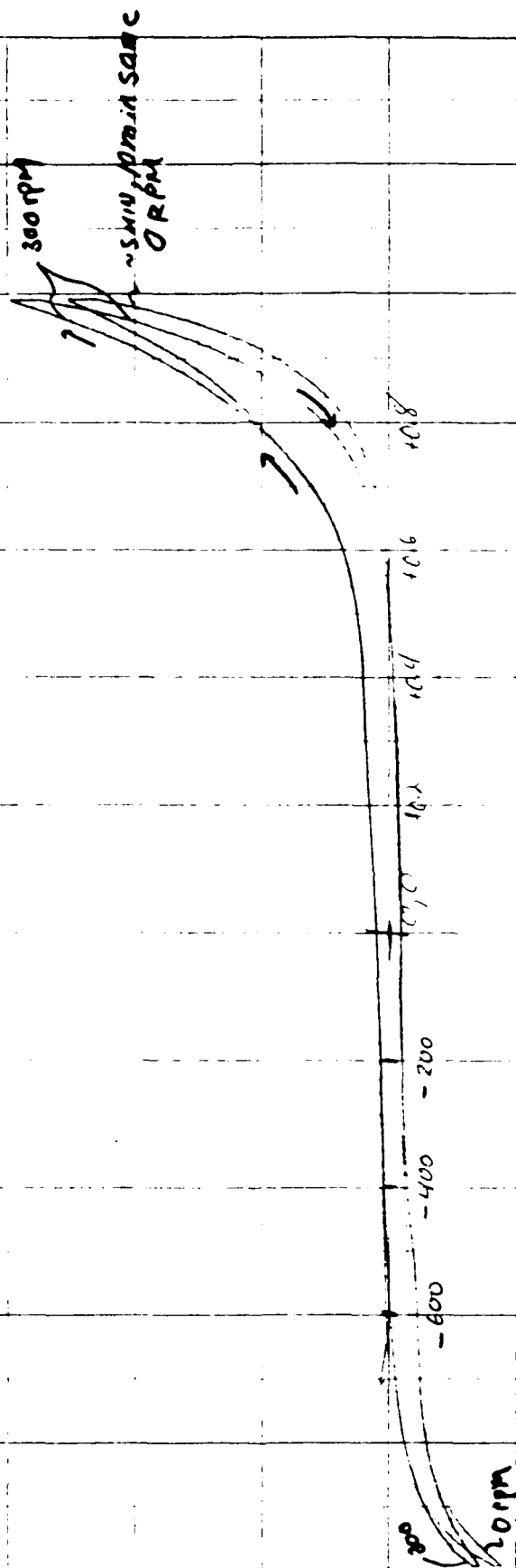
Figure 7. Cyclic voltammetry of a glassy carbon electrode in 2.8-M HAN with various rotation rates

Figure 8. Cyclic voltammetry of a glassy carbon electrode in 2.8-M HAN at various potential scan rates

Run USA-2-PBL-4

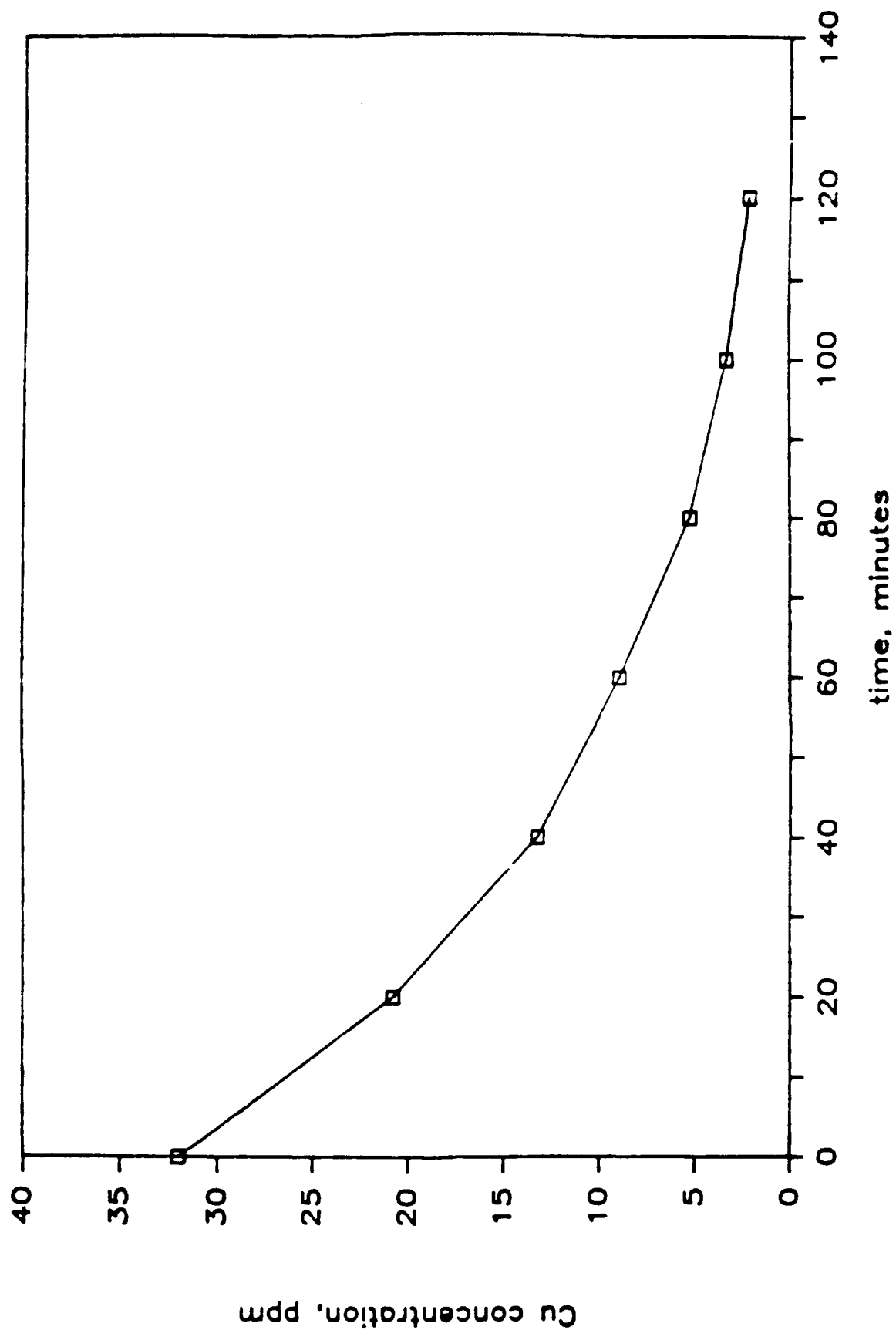Cu concentration, ppm

time, minutes
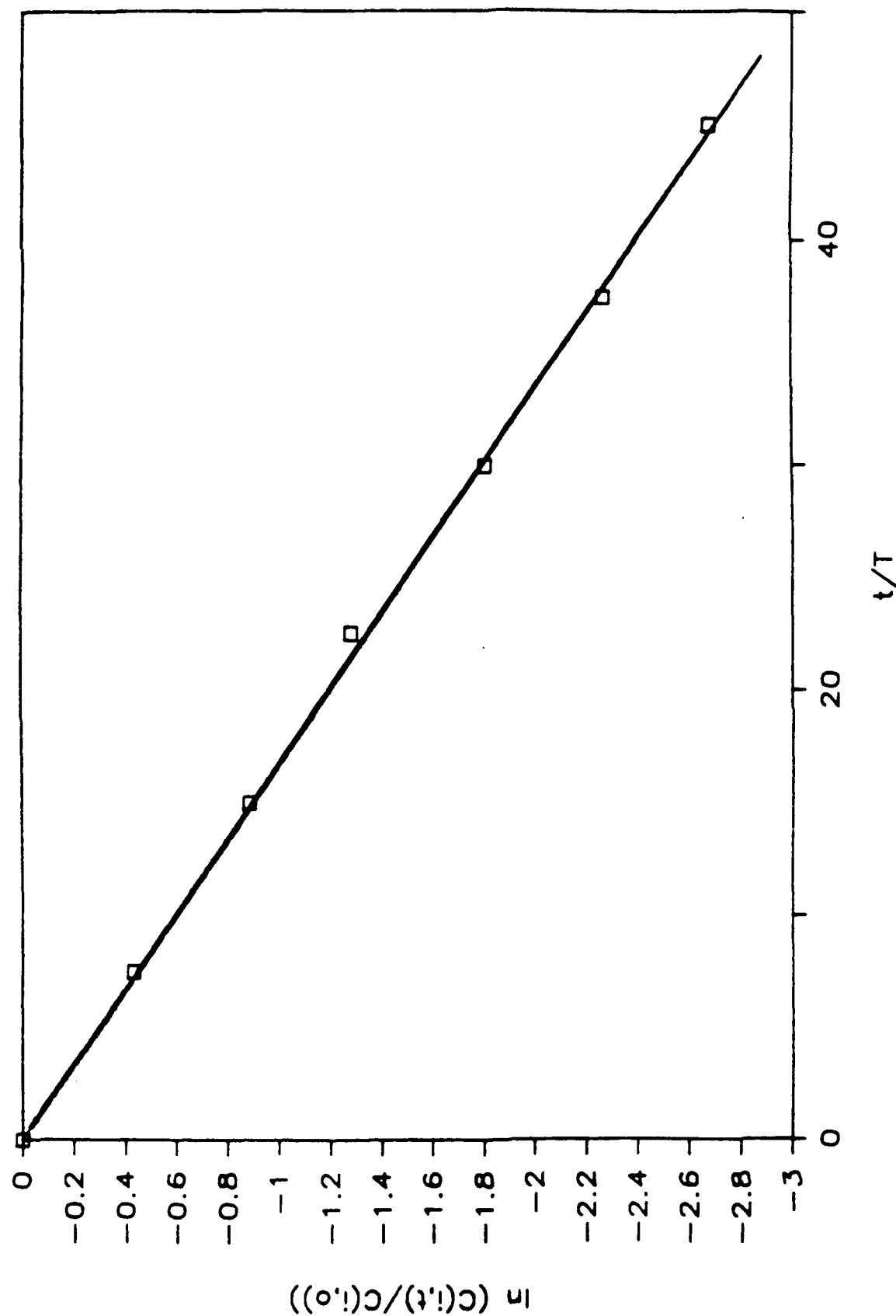
Figure 9 Copper concentration in sump

33

Figure 10. Linearized copper concentration data

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